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In-situ Preparation of Self-assembled Polyaniline/ Poly(styrene sulfonic acid) Composite Ultra Thin Films on Aminosilane Grafted Surfaces

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In-situ preparation method of self-assembled polyaniline (PANI)/ poly(styrene sulfonic acid) (PSS) composite ultra thin films on aminosilane grafted surfaces was proposed. PSS was adsorbed on the aminosilane grafted Si-wafers, then PANI/ PSS composite thin films were prepared *in-situ* by template polymerization utilizing electrostatic interaction between PSS and aniline. PANI/ PSS composite thin films were characterized by time of flight secondary ion mass spectroscopy (TOF-SIMS), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible-near infrared (UV-Vis-near IR) spectroscopy. XPS spectra made it clear that the composition of PANI/ PSS composite thin films was 2/1 mol/ mol. AFM images, XPS spectra, and UV-Vis-near IR spectra revealed that PANI/ PSS composite thin films were selectively prepared on aminosilane grafted Si surfaces.

Key words: PANI/ PSS composite ultra thin film, aminosilane grafted surface, electrostatic interaction.

1. Introduction

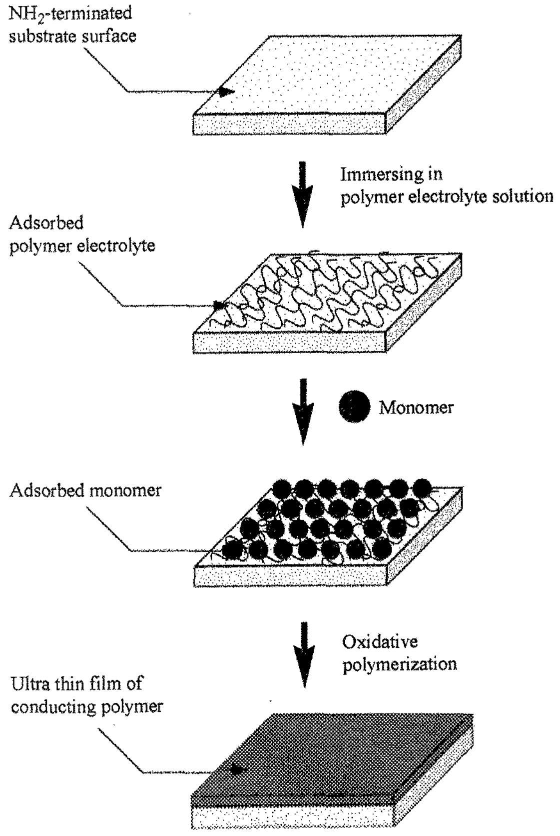
In recent years, PANI has been a tremendous interest since it shows excellent stability, wide range of functional properties, and it is able to be prepared from non-organic solvent system.$^{1,2)}$ Therefore, PANI is expected as new electronic and optical devices which will be substituted for metallic materials. So far, thin films of PANI have been prepared by using 'self-assembly method'. One can prepare the multi-layer of PANI and polymer electrolyte by using this method. $^{2)}$ However, this method needs a large number of process to prepare sufficient film to utilize as electronic devices, and the conductivity of PANI multi-layer film prepared by this method was not greater than 1 S/cm. $^{1)}$

In the present paper, the authors propose a novel PANI ultra thin film fabrication technique named '*in-situ* preparation method'. This method is based on oxidative matrix polymerization.$^{3)}$ Scheme 1 shows the schematic representation of preparation of PANI/PSS composite thin film. Here, the authors report the preparation of PANI/ PSS composite ultra thin films onto the aminosilane self-assembled monolayers (SAMs), and characterization of their composition and physicochemical properties.

2. Experimental Section

2.1 Preparation of PANI/ PSS composite thin films

In order to prepare organosilane SAMs, the presence of Si-OH groups on the substrate surface is necessary to form a chemical bonding between the monolayers and surface of substrates. Si wafer and quartz glass substrates were photochemically cleaned by a vacuum UV/ozone treatment so as to prepare OH-terminated Si substrate surfaces. An excimer lamp (Ushio Electric Co. Ltd., UER20-172V, λ=172 nm) served as the light source.$^{4)}$ The irradiation time was 3 min. Each ethanol 95 % deionized water solution of 3-(2-aminoethylaminopropyl)dimethoxysilane [AADMS, $NH_2(CH_2)_2NH(CH_2)_3Si(OMe)_2CH_3$, Shin-etsu Chemical



Scheme 1 Schematic representation of '*in-situ* preparation method'.

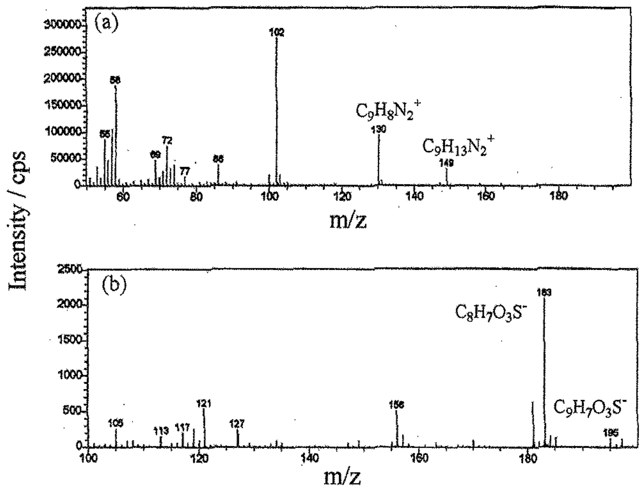


Figure 1 (a) Positive ion and (b) negative ion TOF-SIMS spectra for PANI/ PSS composite ultra thin films.

Co., Ltd.], and *n*-octadecyltriethoxysilane [OTES, $CH_3(CH_2)_{17}Si(OEt)_3$, Chisso Co. Ltd.] was prepared with a concentration of 0.25 M. The acetic acid was added to OTES solution to maintain pH = 4.5 to accelerate hydrolysis. Organosilane SAMs were prepared by immersing the substrates in organosilane solutions for 2 min at room temperature, and then they were rinsed three times with ethanol. After drying substrates immobilized SAMs, the SAMs on substrates were annealed in a vacuum oven at 373 K for 10 min.[5]

The aniline (99 %, Kanto Chemical Co. Ltd.) was purified by vacuum distillation. PSS (30 % in water, Poly Science Co. Ltd.) and ammonium persulfate (98 %, Kanto Chemical Co. Ltd.) were used without purification. All reactions were carried out at 288 K. In advance, to adsorb a large amount of aniline uniformly onto the immobilized PSS layer, the pre-adsorbed PSS layer was prepared by immersing the aminosilane-immobilized substrates in 27 mM PSS aqueous solution for 5 min. Then PSS adsorbed substrates were immersed in 60 mM aqueous solution of PSS, and added equimolar amount of aniline to this solution. The mixture was kept for 12 h. Then aqueous solution of ammonium persulfate, which contained 1/2 molar amount of aniline, was added to the mixture. It took 1 h to complete the addition of ammonium persulfate solution into the mixture. The stoichiometry of all samples is aniline: PSS = 1:1, and the concentration of aniline and PSS were 60 mM. PANI/ PSS composite ultra thin films on substrates were rinsed several times by deionized water and ethanol. The samples were dried in the vacuum desiccator for 5 h.

2.2 Characterization of PANI/ PSS composite thin films

Time of flight secondary ion mass spectroscopy (TOF-SIMS) measurements were carried out by using a PHI TRIFT II (ULVAC-PHI Co. Ltd.) with a 15 keV Ga pulse source which was run at 600 pA with 13 nsec pulse length. The scan was done for 3 min with 10000 pulse/sect . The scan areas were 100 μm square.

XPS spectra were obtained on a PHI ESCA 5800 H (ULVAC-PHI Co. Ltd.) with an Al K_α X-ray source that was run at 14 kV and 24 mA. The pressure in the XPS analysis chamber was maintained at 10^{-9} Torr or lower during data collection. The bonding energies were referenced to the C_{1s} graphite carbon peaks at 284.6 eV in order to correct for the charging energy shift, and the spectra were deconvoluted into suitable components of a Gaussian-Lorentzian function.

UV-Vis-near IR spectra were investigated by using UV-3100 PC (Shimadzu Co. Ltd.). The scan rate was 160 nm min^{-1}, width of slit was 5.0 nm, and the measurement was carried out in the wavelength between 220 nm and 2200 nm.

The surface morphology of PANI/ PSS composite ultra thin films was observed with AFM, which was carried out by using of SPA 300 with SPI 3700 controller (Seiko Instruments Industries Co. Ltd.). AFM observations were carried out at room temperature under constant force mode with a reference force of 0.1 nN. Si_3N_4 rectangular cantilever with a spring constant of 0.09 N m^{-1} was used.

3. Results and Discussion

3.1 Characterization of PANI/ PSS composite thin films

'*In-situ* preparation method' was carried out based on electrostatic interaction among monomer, polymer electrolyte, and surface functional groups. Polymer electrolyte was immobilized on substrate by ionic interaction between positive charge of surface functional groups like protonated NH_2-groups and negative charge of PSS. Then, doped-polyaniline was obtained by using immobilized polymer electrolyte as a template. Therefore,

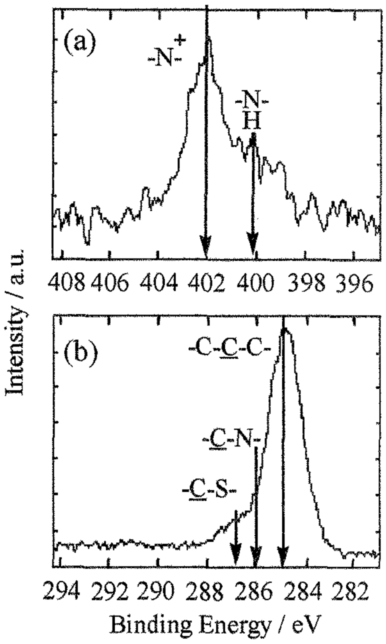


Figure 2 (a) N_{1S} and (b) C_{1S} XPS spectra of PANI/ PSS composite ultra thin films on AADMS SAMs.

Table I Composition of PANI/ PSS composite ultra thin films.

	Ratio of C /N	Ratio of (C-C/C-N/C-S)
observed	10.9/1.0	74/20/6
$[(PANI)_2(PSS)_1]$ (Calcd.)	10.0/1.0	75/20/5

uniform ultra thin film of conducting polymer was prepared on surface functional groups.

To characterize prepared PANI/ PSS composite ultra thin film on AADMS SAMs, TOF-SIMS was carried out. Figure 1 shows TOF-SIMS spectra for PANI/ PSS composite ultra thin films. The detected major peaks were assignable to the fragments of PANI and PSS units. onsidering from these TOF-SIMS spectra, PANI/PSS composite thin films were successfully fabricated on AAMDS SAMs.

To obtain further information about the composition of the films, XPS measurements were carried out. Figure 2 shows the N_{1s} and C_{1s} spectra of PANI/ PSS composite thin films on AADMS SAMs. The peak at 400.1 eV is associated with undoped amine units. The peak at 402.0 eV can be assigned to the protonated amine unit, because the positive charged nitrogen atom attracted core electron to its atomic nucleus by electrostatic interaction.[6] The 284.7 eV, 285.6 eV, and 287.0 eV peaks are C-C, C-N, and C-S bonds, respectively.[6,7] Table I shows the composition of PANI/PSS composite ultra thin films calculated on the basis of XPS.[8] The composition of PANI/ PSS composite thin films was estimated (2/1 mol/mol), which gave good agreement with the calculated value based on the chemical structures.

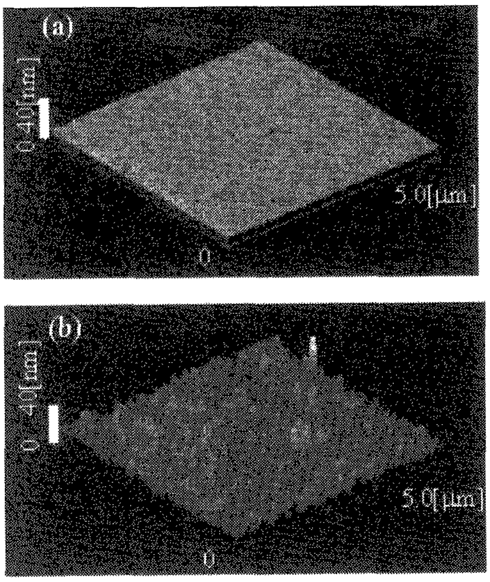


Figure 3 AFM 3D images for PANI/ PSS composite ultra thin films on (a) AADMS and (b) OTES SAMs.

3.2 Surface-selective formation of PANI/ PSS composite ultra thin films

To confirm the formation of PANI/ PSS composite ultra thin films, AFM observation was carried out for the films on AADMS and OTES SAMs. Figure 3 shows the AFM 3D images of PANI/ PSS composite ultra thin films on (a) AADMS and (b) OTES SAMs. PANI/ PSS composite ultra thin films formed uniform surfaces on AADMS SAMs. The thickness of this uniform film was estimated about 16 nm by AFM measurement. On the other hand, PANI/ PSS composite ultra thin films formed granular structures on OTES SAMs. These results suggested that the formation of PANI/PSS composite thin films strongly depended on the surface functionality of the substrate.

The difference of electrostatic characteristic of PANI/ PSS composite thin films was also confirmed by in N_{1s} XPS spectra (Figure 4). N_{1S} XPS spectra shows that compared with OTES SAMs, the area% of component attributed to protonated nitrogen was larger on AADMS SAMs, which shows the higher degree of protonation of PANI. The increase in continuity of conjugation bonds of PANI on AADMS SAMs was confirmed on the basis of UV-Vis-near IR spectra. Figure 5 shows absorption at λ=780 nm was attributed to polaron band in PANI/ PSS composite thin films.[1] The long tail from λ=780 nm was suggested the progress of conjugation of PANI. The intensity of absorption at λ=780 nm of (a) was about 4.5 times as strong as (b). It is well known that the absorption of polaron band was observed at highly conjugated conducting polymer. These spectra suggested that the advance of formation of highly conjugated PANI/PSS composite ultra thin films on AADMS SAMs.

In considering these results, the formation of uniform

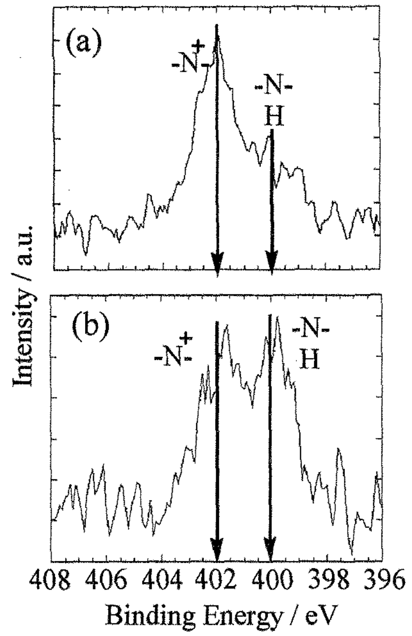


Figure 4 N_{1S} XPS spectra for PANI/ PSS composite ultra thin films on (a)AADMS and (b) OTES SAMs.

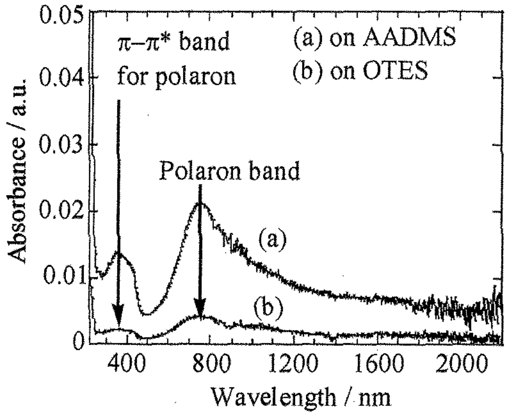


Figure 5 UV-Vis-near IR spectra for PANI/ PSS composite ultra thin films on (a)AADMS and (b)OTES SAMs.

PANI/ PSS composite ultra thin films is closely related with electrostatic character of functionalized substrate surfaces. The AADMS SAMs have positive charged surfaces.

The amount of PSS on AADMS SAMs was larger than that on OTES SAMs.[2] In '*in-situ* preparation method', PSS plays an important role as template for polymerization of aniline. Therefore, the positively charged surfaces facilitated the formation of PANI/ PSS composite thin films on AADMS SAMs. On the other hand, PANI/ PSS composite ultra thin film was scarcely formed on the OTES SAMs because of the lack of electrostatic interaction.

Conclusion

In conclusion, the authors succeeded in preparing the PANI/ PSS composite ultra thin films on aminosilane grafted Si surfaces by '*in-situ* preparation method'. The composition of the obtained films was estimated to be PANI/ PSS = 2/1 mol/mol. The protonation of nitrogen and surface morphology of PANI/ PSS composite thin films depended on the electrostatic interaction between PSS and surface functional groups of the substrates. In the case of aminosilane grafted Si surfaces, adsorption of PSS was proceeded by the positively charged surface. Therefore, uniform and highly doped PANI/PSS composite ultra thin films were prepared on AADMS SAMs. By this method, one can easily prepare the uniform self-assembled thin films immobilized on the substrates

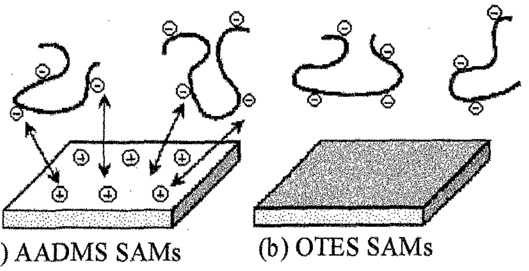


Figure 6 Schematic representation of adsorption of PSS onto (a)AADMS and (b)OTES SAMs.

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